(iii) It follows, therefore, that the piezoelectricity is related to crystal symmetry. The symmetry element involved is essentially the centre of inversion. A crystal can exhibit piezoelectricity only if its unit cell *lacks a centre of inversion*. In fig. 9(a), crystal has no centre of inversion but if fig 9(b) there is. That is why in fig. 9(a) charge distribution is distorted so as to produce polarization whereas in fig. 9(b), no charge distortion.

Piezoelectricity is thus exhibited by only non-centrosymmetric systems. 21 out of 32 crystal classes are non-centrosymmetric. The absence of centre of symmetry makes it possible for crystals in these classes to have one or more directions of polarisation under stress.

Piezoelectric effect is extensively used to convert electrical energy into mechanical energy and *vice versa*, *i.e.*, piezoelectric substances are used as electro-mechanical transducers. Another important application of piezoelectricity is their use as highly stable oscillators for frequency control.

14.6 FERROELECTRICITY*

There are certain dielectric substances, called ferroelectrics, which have the following typical properties :

(i) For most of the substances, it is true that ionic susceptibility is not sensitive to variations in temperature but for ferroelectric class of materials, static dielectric constant changes with temperature according to the relation

$$\varepsilon_r = B + \frac{C}{T - T_c} \quad ; \quad T > T_c \qquad \ldots(1)$$

where B and C are constants, independent of temperature. This relation is called *Curie-Weiss law*. C is called *Curie constant* and T_c, the *Curie temperature*. Relation (1) is shown by a plot in ε_r and T in fig. 10(a). For $T < T_c$ the above behaviour does not hold good.

(ii) In the temperature range $T < T_c$, the material becomes *spontaneously polarised*, *i.e.*, an electric polarisation develops in it *without the help of an external field* (even when no external field is present, the centres of gravity of the positive and negative charges are separated and electric polarisation is spontaneously induced). Thus at T_c, a phase transition occurrs; above T_c the substance is in *paraelectric phase* in which elementary dipoles are randomly oriented but below T_c, the dipoles interact

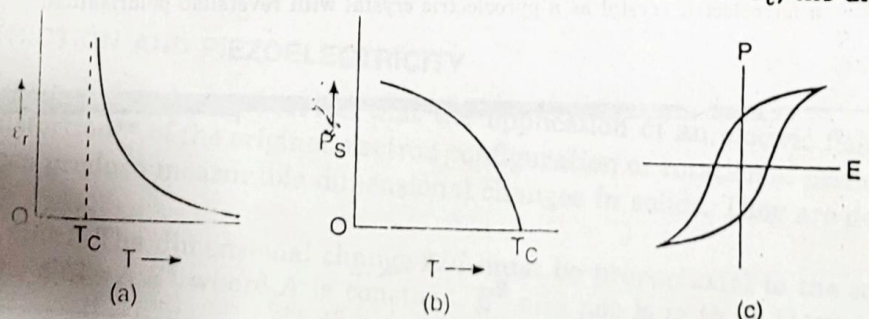

Fig. 10. (a) Dielectric constant versus temperature curve.
(b) Spontaneous polarisation versus temperature curve.
(c) Hysteresis loop.

* Nature of electric properties of matter can be known from the distribution of charges in the unit cell just as the magnetic properties of matter can be understood from the distribution of currents in the unit cell.

with each other. Their interaction gives rise to an internal field, which lines up the dipoles. Thus the process of spontaneous polarisation arises. This polarisation increases gradually as the temperature is lowered [fig. 10(b)].

(iii) Characteristic of a ferroelectric substance is that the polarisation is not fixed in a certain definite direction of the crystal; when a sufficiently strong electric field is applied, the polarisation direction can be reversed. That is, crystal polarisation will show hysteresis in alternating fields. Thus property is called ferroelectricity after a similar phenomenon in magnetism. (In fig. 10(c), a polarisation *versus* electric field curve is shown. It is ferroelectric hysteresis loop—quite similar in shape to *B-H* curve of a ferromagnetic material.

(iv) Spontaneous polarisation and hysteresis are thus the essential characteristics of ferroelectric substances.

Barium titanate $BaTiO_3$ is the most familiar ferroelectric substance. Rochelle salt, NaK $(C_4H_4O_6) \cdot 4H_2O$ (potassium-sodium tartrate) is another common example. Many other discovered ferroelectrics are : the ammonium sulphate $(NH_4)_2 SO_4$ group, the guanidine chemical compounds, the triglycine sulphate group and the potassium ferrocyanide trihydrate group; many of them possess complicated crystal systems and hydrogen bonds.

Theories of ferroelectricity : As said earlier, spontaneous polarisations* and hysteresis are the essential characteristics of ferroelectric substances. In connection with these characteristics we may make the following observations :

(i) The state in which a crystal has spontaneous polarisation is a state which has a low symmetry. When an external field is applied, the crystal makes a transition to another state of a low symmetry (a state in the 'reversed direction') due to the action of the field, but the crystal must pass through an intermediate state—a non-polar state of higher symmetry.

(ii) In ferroelectric substances, the aforesaid non-polar state is more stable at high temperatures, and at a certain definite temperature, there occurrs a phase transition from a state having spontaneous polarisation to a state having no spontaneous polarisation. This is called transition temperature (the Curie temperature, T_c).

(iii) Above the transition, the dielectric constant obeys the Curie-Weiss law

$$\varepsilon_r = \frac{C}{T - T_c}$$

In the neighbourhood of the transition temperature**, ε_r is extremely large. Below transition temperature, the dielectric constant decreases abruptly but still assumes a large value. Such a transition is a characteristic of all ferroelectric substances.

Dielectric behaviour above T_c : Based on the assumption that a ferroelectric substance consists of a system of freely rotating dipoles, a dipole theory (analogous to Langevin-Weiss theory of ferromagnetism)—which uses the Lorentz local field, seems to be an obvious theory of ferroelectricity. For high temperature region, the theory leads to Curie-Weiss law

$$\varepsilon_r = \frac{C}{T - T_c} \qquad ...(1)$$

This relation has been obtained by using a dipolar model, neglecting electronic and ionic contributions and it predicts that ε_r diverges as $T \to T_c$ from above. As a result, the system

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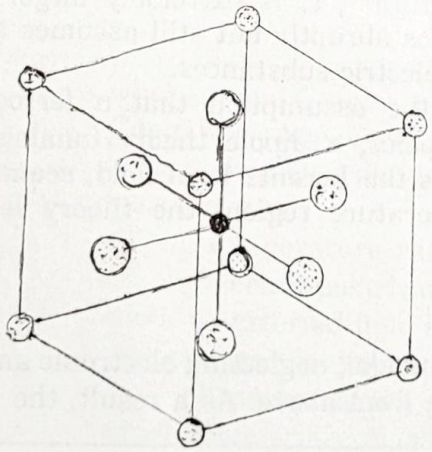
* We talk of spontaneous polarisation in ferroelectricity as there is discussion of a phenomenon of spontaneous magnetisation in ferromagnetism.

** It is 120°C for barium titanate.

seems to become unstable and make a transition to a new phase, the *ferroelectric phase*. This model predicts that water would become ferroelectric at $T_c = 1100$ K but water, in fact, never becomes ferroelectric. Thus this model is inadequate to account for observations.

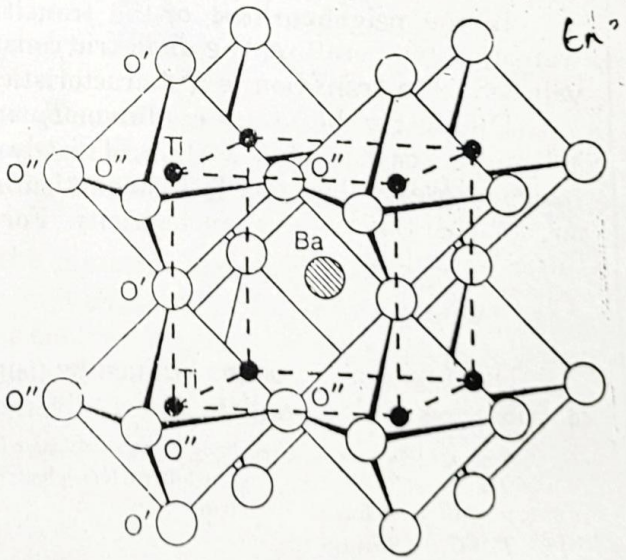
We proceed with the description of barium titanate $BaTiO_3$ about which most experimental and theoretical information is available. It has the simplest crystal structure the perovskite structure (the name perovskite applies to the mineral $CaTiO_3$)*. The structure (fig. 11) is cubic, with Ba^{2+} ions at the cube corners, O^{2-} ions at the face centres, and a Ti^{4+} ion at the body centre. The single titanium ion is surrounded by six oxygen ions all equidistant from it, and is therefore at the centre of cubic symmetry, whereas the oxygen ions are not at positions of cubic symmetry. This structure is above T_c because below T_c, the structure is slightly deformed with respect to that described here (refer to next subarticle - spontaneous polarisation below T_c).

The occurrence of ferroelectricity in a barium titanate is believed to be the result of a polarisation catastrophe in which the local electric fields arising from the polarisation itself increase faster than the elastic restoring forces on the ions in the crystal, thereby leading ultimately of an asymmetrical shift in ionic positions; the shift is limited to a finite displacement by the onset of anharmonic restoring forces. We now give the simple form of the catastrophe theory, supposing that the Lorentz factors are all $4\pi/3$. Refer to Clausius Mossotti relation [eq. (9) art. 14.3]



(a)

Fig. 11(a). The perovskite crystal structure of barium titanate. The structure is cubic with Ba^{2+} ions at the cube corners O^{2-} ions at the face centers, and a Ti ion at the body center. Below the Curie temperature the structure is slightly deformed with respect to that described here. The prototye crystal is calcium titanate (perovskite).



(b)

Fig. 11(b). The $BaTiO_3$ structure, showing the octahedra of oxygen atoms about the titanium atoms. The oxygen atoms on the lines joining nearest neighbour titanium atoms are labeled O'.

* $SrTiO_3$ is a cry[illegible] of perovskite as $BaTiO_3$, but is not ferroelectric.

$$\varepsilon_r = \frac{1 + \frac{8\pi}{3} \sum_i n_i \alpha_i}{1 - \frac{4\pi}{3} \sum_i n_i \alpha_i} \qquad \ldots(2)$$

where α_i is the polarisability of an ion of type, i, and n_i the number of ions, i, per unit volume [note that we have modified eq. (7A) art. 14.3 by taking Lorentz local field $\mathbf{E}_{in} = \mathbf{E} + \frac{4\pi}{3}\mathbf{P}$, into the above form]. We note that dielectric constant, ε_r, becomes infinite, corresponding to a finite polarisation for zero applied field, $\Sigma\, n_i\, \alpha_i = (4\pi/3)^{-1}$, and for this reason the polarisation catastrophe is commonly known as the '$4\pi/3$' catastrophe.

The value of ε_r is sensitive to small departures of $\Sigma\, n_i\, \alpha_i$ from the critical value $3/4\pi$; if we write

$$\left(\frac{4\pi}{3}\right) \sum_i n_i \alpha_i = 1 - s, \qquad \ldots(3)$$

where $s \ll 1$; we have from equation (2) that

$$\varepsilon_r \simeq 3/s \text{ (neglecting } 2s \text{ in the numerator as } s \ll 1) \qquad \ldots(4)$$

If we suppose that, near the critical temperature, the value of s varies with temperature in a linear fashion,

$$s \equiv \beta(T - T_c)\,,$$

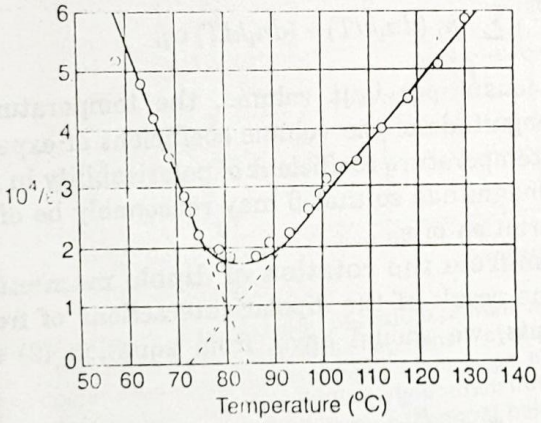


Fig. 12. Plot of reciprocal of the dielectric constant of barium titanate vs temperature, after B. Wul. Curie point is 40°C below that reported by other workers* (see Fig. 13).

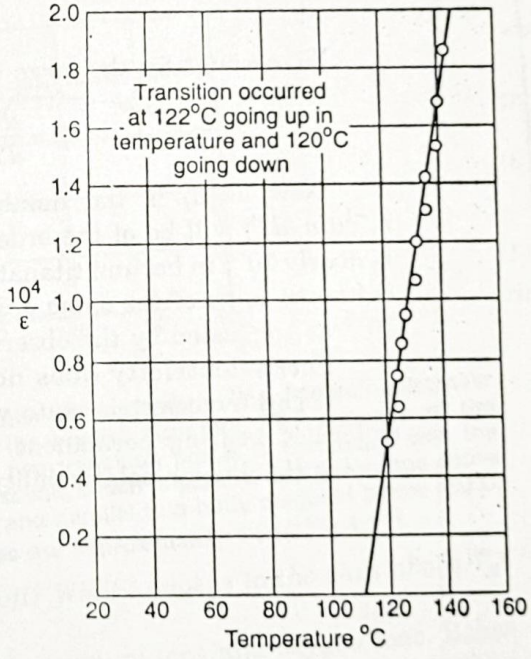


Fig. 13. Reciprocal dielectric constant of barium titanate vs temperature (After Drougard and Young). A more recent work.

* Perhaps due to substantial quantity of impurities being present which might have affected the nature of phase transition, making it appear to be second order transition, whereas transition is actually first order.

where β is a constant; we have above the transition temperature a Curie-Weiss law for the dielectric constant given by

$$\varepsilon_r = \frac{3/\beta}{T - T_c} \qquad ...(5)$$

which is of the form of the observed temperature variation, as shown in fig. 12 and fig. 13. From observed variation

$$\varepsilon_r = \frac{10^5}{T - T_c} \qquad ...(6)$$

To account for the large value of the numerator observed in equation (6), we note that

$$\beta = \frac{ds}{dT} = \left(\frac{4\pi}{3}\right) \sum [n_i (d\alpha_i/dT) + (dn_i/dT)\, \alpha_i]$$

Now as n_i is the number of ions i per unit volume, the temperature coefficient $n_i^{-1}(dn_i/dT)$ will be of the order of magnitude of the volume coefficient of expansion, which is nearly 10^{-5} in barium titanate; the temperature coefficient of polarisability in ionic crystals is known to be of the same order of magnitude so that β may reasonably be of the order of 10^{-5} as suggested by the observed variation of ε.

Ferroelectricity does not arise from the rotation of dipole moments :

If the ferroelectric state were the result of the dipolar interactions of freely rotating molecules bearing permanent moments, we should have, from equation (9) art. 14.3 on putting the dipolar polarizability :

$$\alpha = \frac{p^2}{3 K_B T}$$

that

$$\varepsilon_r = \frac{3 T_c}{T - T_c}, \qquad ...(7)$$

where† $T = \dfrac{4\pi n p^2}{9 K_B} \approx 1200$ K.

In equation (7), numerator $3T_c \approx 10^3$ K is two orders of magnitude smaller than the observed due of 10^5 in equation (6). This failure is a strong indication that we are not concerned in barium titanate with the orientation of molecules bearing permanent dipole moments. *In fact ferroelectricity arises, not from rotation, but from vibration states; the displacement of certain ions from their equilibrium positions strongly unbalances the equilibrium of the permanent moments. By a proper structural arrangement, this upset induces a motion of the neighbouring ions in a supporting sense which increases the original displacement by feedback. The tendency to bring the vibrations of neighbouring ions into ordered phase relations prevails at the Curie point against the random agitation, and the equilibrium position of the critical ions shifts to one side since the whole effect was made possible on by the displacement of these ions. The old balance of the permanent moments is destroyed and a polar axis created by the transformation of induced moments into permanent moments.*

† Using dipole moment of 1·87 Debye units, we may estimate T_c for water

$$T_c = \frac{(12{\cdot}6)\,(6{\cdot}03 \times 10^{23}/18)\,(1{\cdot}87 \times 10^{-18})^2}{9\,(1{\cdot}38 \times 10^{-16})} = 1200 \text{ K}$$

Spontaneous polarisation below T_c : We know that the property of ferroelectricity associated essentially with asymmetric ionic displacements in the crystal structure. Above the structure of barium titanate is shown in fig. 11. In order to explain spontaneous polarisation, P_s, of it, we have to study the changes in its crystal structure as it is cooled through T_c. Refer to fig. 11. We note that structure of $BaTiO_6$ is cubic :

(i) with each of the Ti^{4+} ions surrounded by six O^{2-} ions in an octahedral configuration,

(ii) the TiO_6 octahedron is symmetrical, and

(iii) the centre of gravity of the negative charges is coincident with that of the positive charges. The net dipole moment is, therefore, zero.

As it is cooled through T_c, the Ti^{4+} and Ba^{2+} ions move with respect to the O^{2-} ions; the *X*-ray and neutron diffraction data show that titanium and barium ions all move up 5 percent and the oxygen ions move down 1 percent. The structure is now tetragonal (c/a ratio 1·04) with no centre of symmetry, and the centre of gravity of negative charges is *no longer coincident* with that of positive charges. This situation obviously leads to a spontaneous dipole moment and consequent spontaneous polarisation of the crystal arises, (fig. 14). Thus ferroelectricity can occur only in those *non*-centrosymmetric crystals which provide a favourable axis of polarisation. Only 10 crystal classes satisfy these requirements.

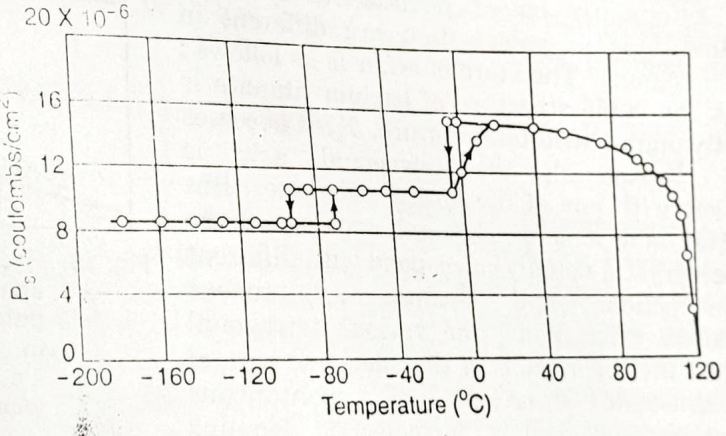


Fig. 14. Spontaneous polarization of barium titanate as a function of temperature. The discontinuities near 0°C and −80°C are caused by small changes in the crystal structure. The changes of the polarization measured along a cube edge at these two transition points is consistent with the assumption that the direction of spontaneous polarization, which is parallel to a cube edge above 0°C, becomes parallel to a face diagonal below 0°C and parallel to a body diagonal below −80°C, as the ratios of the P_s at the transition temperatures are approximately $1 : 1/2^{1/2} : 1/3^{1/2}$.

Why below Curie temperature (T_c) there is a shift? What happens to the shift above T_c?

The reason for this may be stated as follows :

That there exists a strong coupling between the titanium ions and oxygen ions. Below Curie temperature, the titanium ion is displaced towards one of six oxygen ions, rather than being equally distant from all, upsetting the symmetry and providing a favourable axis of polarisation. But above Curie temperature, the thermal energy of the crystal lattice becomes high enough to make all the six possible equilibrium positions of the titanium ion equally probable, and thus fix, in an average sense, the titanium ion at the centre of the TiO_4 octahedron, leading to centre of symmetry.

Ferroelectric Hysteresis (Ferroelectric Domains) : Just like in ferromagneti there are domains that explain the *B-H* curve (hysteresis), here too there are *ferroelectric domains* (as confirmed by *X*-ray and optical studies). That is, specimen is divided into certain polarised regions such that the *directions of polarisation are different in different directions. These regions are called ferroelectric domains.* How directions of polarisation are different in different regions? The state of affair is as follows :

As the cubic structure of barium titanate is cooled through Curie temperature, T_c, it becomes slightly tetragonal; the tetragonal axis is coincident with one of the former cube axes. But the tetragonal axis of different regions of the specimen crystal usually correspond with different cube directions and because spontaneous polarisation exists along the various tetragonal axis, the different regions of the specimen crystal have different directions of spontaneous polarisation. That is how ferroelectric domains arise.

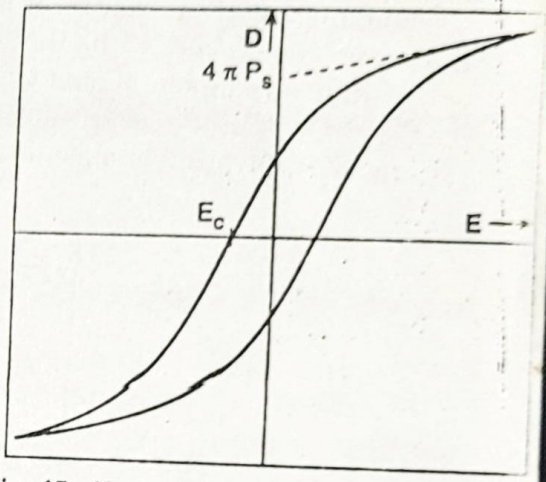


Fig. 15. Hysteresis loop in ferroelect specimen, showing spontaneo polarization P_s and coercive field In barium titanate the value $4\pi P_s$ may be of the order of 3×1 v/cm, and E_c of the order of 10^3 v/c

If an electric field is applied to a domain structure, then

(i) domains that are favourably oriented with respect to field direction may grow at the expense of less favourably oriented domains, and/or

(ii) the direction of polarisation may rotate towards the direction of field.

This implies that polarisation of the specimen crystal will change with electric field an if the electric field is alternating, polarisation direction is reversed, exhibiting th phenomenon of hysteresis (fig. 15). Properties of some ferroelectric materials is listed i table 2.

Table 2. Properties of some ferroelectric materials.

Material	Chemical formula	P_s coulombs/m^2	T_c, °C
Rochelle salt	$KNaC_4H_4O_6 \cdot 4H_2O$	$0{\cdot}24 \times 10^{-2}$	upper + 24, lower − 18
KDP	KH_2PO_4	4·95	− 150
Potassium niobate	$KNbO_3$	3·78 (at 410°C)	+ 434
Barium titanate	$BaTiO_3$	26·0 (at 23°C)	+ 120

Applications of ferroelectricity :

(i) The dielectric constant of ferroelectrics is very high (thousands or many thousands in a number of cases) and so they are used in manufacture of small size high capacity capacitors.

(ii) The property of hysteresis makes it possible to use them as memory devices for computers, and

(iii) Piezoelectric acoustic transducers and pyroelectric infrared detectors are the devices based also on ferroelectrics.

(iv) The electro-optic characteristics of ferroelectrics such as $BaTiO_4$ and KDP have been used for modulating and deflecting laser beams both inside and outside the optical cavity.

Ferroelectricity and Piezoelectricity :

(i) Both the phenomena occurr in non-centrosymmetric crystals which are 20 in number. Piezoelectricity occurrs in all 20 crystals, whereas ferroelectricity only in 10, namely, those which provide a favourable axis of polarity. Thus all ferroelectrics are piezoelectric but all piezoelectrics are surely not ferroelectric, *e.g.*, tourmaline is piezoelectric but not ferroelectric.*

(ii) In piezoelectricity, the crystal is polarised by the application of an external stress, whereas in ferroelectricity the source of polarisation is the dipole interaction energy itself.

(iii) The piezoelectric coefficients is the ratio of the set-up charge to the stress applied. The ferroelectrics have very large piezoelectric coefficients.

Ferroelctricity and ferromagnetism :

In the ferromagnetism, whenever the moments are spontaneously aligned, they can also be reversed by means of an external field. On the other hand, in ferroelectricity, the moments must be loosely aligned. *i.e.*, the interaction must be so delicately balanced so as to allow reversal of the spontaneous polarisation, for otherwise, we get pyroelectricity. This loose alignment will be disturbed by rising temperature. Hence most ferroelectrics have a transition temperature above which they are normal and non-polar. It means a crystal in the ferroelectric phase must be of lower symmetry than in the nonpolar phase.

14.7 ANTIFERROELECTRIC CRYSTALS

Some interactions in ionic crystals lead to a type of spontaneous polarisation termed as antiferroelectric. Unlike the ferroelectrics, antiferroelectrics have no permanent moment, because of the geometry of the spontaneous polarisation. They are the crystals having lines of ions spontaneously polarised—but with neighbouring lines polarised in antiparallel directions. If the polarisation in one direction is equal to that in the other, the net polarisation is zero. These solids (table 2) have an antiferroelectric Curie temperature, T_c, above which the effect does not exist. They have a relative capacitivity somewhat larger than that of the normal dielectric.

For the common antiferroelectrics ε_r is of order 50 to 150. Some antiferroelectric compounds are listed in the table 3.

Table 3. Properties of some antiferroelectric materials.

Material	Composition	T_c °C
ADP	$NH_4H_2PO_4$	− 125
Sodium niobate	$NaNbO_3$	+ 638
Lead zirconate	$PbZrO_3$	+ 233

* Though its relative strength of piezoelectric coefficients is small whereas that of Rochelle salt is very large. Rochelle salt is both piezoelectric and ferroelectric.